Geometry-induced smoothing of van Hove singularities in capped carbon nanotubes

D.V. Kolesnikov[1] and V.A. Osipov[2]
Joint Institute for Nuclear Research, Bogoliubov Laboratory of Theoretical Physics, 141980 Dubna, Moscow region, Russia
e-mail: [1]*kolesnik@theor.jinr.ru,* [2]*osipov@theor.jinr.ru*
(22 December, 2006)

The electronic states of capped semi-infinite nanotubes are studied within the phenomenological gauge field-theory model. A single manifold for the description of both the nanotube and the cap region (considered as nearly a half of either Ih or I fullerene) is suggested. The wavefunctions and the density of states (DoS) are numerically calculated for both metallic and semiconducting nanotubes. The smoothing of van Hove singularities is found and proven analytically. The comparison with the experimental observations is discussed.
PACS: 73.22.-f, 71.20.Tx, 73.22.Dj

The electronic properties of capped carbon nanotubes are essential to proposed device applications. The localized eigenstates in a cap region were predicted theoretically in [1]. Experimentally, the signature of resonance states localized at the ending caps of a nanotube was observed in the spectroscopic measurements on carbon nanotube caps [2]. Another spectroscopic analysis of carbon caps performed in [3] shows spatially resolved electronic properties along capped nanotubes and highlights the van Hove singularities (VHS) in nanotube bulk and resonance states at the end. The scanning tunneling spectroscopy (STS) gives information about the local density of states (LDoS). Several sharp peaks experimentally observed in [3] were attributed to the VHS. The tight-binding calculations show good agreement with the experimental data (see, e.g., [3,4]).

The aim of our paper is twofold. First, we suggest an appropriate geometry for the shape of capped nanotubes and develop a continuum field-theory model to describe the electronic states. Second, we perform numerical calculations to obtain the structure of DoS. This study gives us an important information about the influence of the cap region on the electronic properties of the nanotube and illuminates the behavior of the VHS. We will consider a closed semi-infinite nanotube with a spherical cap. It is suggested that the nanotube region is defect free (contains only hexagons) and infinitely long, so that edge effects are negligible. The cap is a half of the spherical (I or Ih) fullerene and contains exactly six pentagons. A continuum field-theory model for the description of low-energy electronic states in carbon nanostructures of arbitrary geometry was formulated in [5] in the form

$$-i\sigma^{\alpha}e_{\alpha}^{\ \mu}(\nabla_{\mu}-ia_{\mu}^{k}-iW_{\mu})\psi^{k}=E\psi^{k}. \tag{1}$$

Here σ^{μ} are the conventional Pauli matrices ($\mu=1,2$), the energy E is accounted from the Fermi energy, the Fermi velocity V_F is taken to be one, and the two-component wave function ψ represents two graphite sublattices (A and B). By using the index k in (1) we take into account electronic states at two independent Fermi wave vectors in carbon lattice (so-called "K-spin up" ($K^{\uparrow}$) and "K-spin down" ($K^{\downarrow}$) states). Geometry is involved via zweibeins e_{μ}^{α}, $\nabla_{\mu}=\partial_{\mu}+\Omega_{\mu}$ where the spin connection term $\Omega_{\mu}=(1/8)\omega_{\mu}^{\alpha\ \beta}[\sigma_{\alpha},\sigma_{\beta}]$, and $(\omega^{\mu})^{\alpha\beta}$ are the spin connection coefficients:

$$(\omega_{\mu})^{ab}=e_{\nu}^{a}(\partial_{\mu}e^{\nu b}-\Gamma_{\mu\chi}^{\nu}e^{\chi b})=-(\omega_{\mu})^{ba}, \tag{2}$$

where

$$\Gamma_{\mu\lambda}^{\nu}=\frac{g^{\nu\chi}}{2}(\partial_{\mu}g_{\chi\lambda}+\partial_{\lambda}g_{\chi\mu}-\partial_{\chi}g_{\mu\lambda}) \tag{3}$$

are the metric connection coefficients.

In order to take into account pentagons in the cap region, two compensating gauge fields a_{μ} and W_{μ} are introduced in (1). The Abelian field W_{μ} is responsible for the elastic flux due to pentagonal defect [6,7]. Its circulation around a single disclination is found to be exactly $2\pi/6$ (the appearance of a pentagon in the honeycomb lattice is equivalent to the creation of 60° disclination). The non-Abelian field $\vec{a}$ allows us to take into account the exchange between A and B sublattices in the presence of a pentagon [8,9,5]. Namely, this exchange can be described by using an appropriate boundary condition for the K spin part of the four-component spinor wavefunction $\psi=(\psi^{\uparrow}\psi^{\downarrow})^{T}$ in the form $\psi(\varphi+2\pi)=-T\psi(\varphi)$. Here the holonomy operator T is composed as a product of two operators in the form $\exp(i\Phi\tau_i)$, i=2,3 where the isospin Pauli matrices τ act on the K part of the spinor components. The general consideration takes proper account of the relative placement of pentagons. For even number of defects one has (see [9])

$$\oint a_{\mu}^{k}dx^{\mu}=\pm(N\frac{2\pi}{4}+M\frac{2\pi}{3}). \tag{4}$$

Here the sign plus (minus) is taken for $k = K^{\uparrow}$ ($k = K^{\downarrow}$), respectively, N is a number of defects and M ($M = n-m$ (mod 3)) depends on the arrangement of pentagons, n and m are the numbers of steps in positive and negative directions, respectively. The directions rotated by $2\pi/3$ are considered to be identical. For (I) fullerenes $M = M_2 = \pm 1$ or 0 for any two defects, $M_4 = 0$ for any four defects, and $M_6 = -M_2$ for six defects. In the case of (Ih) fullerenes M is always equal to zero due to the mirror symmetry of the lattice (see [5]).

In the isospin space, the action of the operator T corresponds to a rotation by $2\pi N/4$ around the second axis and then by $2\pi M/3$ around the third axis. The angle between the initial and final vectors gives exactly the phase (4). Notice that for odd number of defects the first transformation places the vector on the third axis, so that the second transformation does not change the angle (phase). To simplify a problem, let us introduce an effective field for uniformly distributed defects instead of six point-like fluxes due to pentagons in such a way that the phase factors in (4) remains the same. Let Γ_S be the circle on the (hemi)sphere (with the unit radius, for simplicity) which encircles the area S including the pole (see fig. 1). Evi

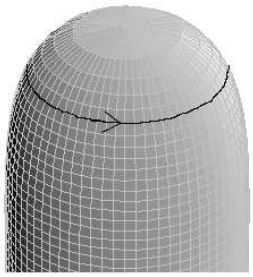

FIG. 1. The modelled geometry of closed tube. A contour Γ_S encircles the surface S. The z-axis is directed downside.

It is easy to find that the operator of rotation around the second axis in the isospace takes the form $\exp(i\tau_2 S3/2)$. Indeed, we have six defects (each rotating on $2\pi/4$) continuously distributed on the area 2π. The rotation angle is $\Phi_M = 3S/2$. The operator of rotation around the third axis can be approximated as $M(S) = -M_2 \cos(3(S-2\pi)/4)$. This agrees with the properties of M described above: $M(2\pi/3) = M_2$, $M(4\pi/3) = 0$, $M(2\pi) = -M_2$. The rotation angle is written as

$$\Phi_T = -\frac{2\pi}{3} M_2 \cos(3(S-2\pi)/4). \tag{5}$$

The total operator T in the form

$$T = \exp(i\tau_3 \Phi_T) \exp(i\tau_2 \Phi_M) \tag{6}$$

corresponds to the phase rotation by angle Φ which is determined from the equation

$$\cos\Phi(S) = \cos\Phi_M(S) \cos\Phi_T(S). \tag{7}$$

As a final step, the circulation of the field $\vec{a}$ along Γ_S is

$$\oint_{\Gamma_S} a_\mu \, dx^\mu = \pm\Phi(S). \tag{8}$$

On the equator of the sphere the circulation is $\Phi(2\pi) = 3\pi + 2\pi M_2/3$. Since the equator is connected with the tube region, any contour around the tube encircles the same quantity of the field sources as $\Gamma_{2\pi}$. Therefore, finally in the spherical region and on the tube we obtain the following conditions:

$$\oint_{\Gamma_S} a_\varphi d\varphi = \pm\Phi(S), \tag{9}$$

$$\int_0^{2\pi} a_\varphi d\varphi = \pm(3\pi - 2\pi M_2/3). \tag{10}$$

Notice that the factor 3π in (10) can be excluded by the redefinition of the momentum j (see below), so that the circulation in the tube region (10) is determined by M_2 in agreement with [10]. For both (Ih) fullerenes and (I)

fullerenes with $M_2 = 0$ one has $\Phi = \Phi_M = 3S/2$, which agrees with monopole approximation [11,5]. Therefore, one can conclude that metallic tubes can be capped by either (Ih) fullerenes (armchair) or (I) fullerenes with $M_2 = 0$ while the semiconducting tubes are capped only by (I) fullerenes with $M_2 \neq 0$.

In the spherical region, the circulation of the field W_φ has the standard form similar to [5]

$$\oint_{\Gamma_S} W_\mu dx^\mu = -S,$$

whereas in the tube region its circulation is equal to -2π and may be ignored.

The continuum description in (1) implies a single manifold with the curvature being a continuous smooth function. Therefore we have to propose appropriate geometry for the capped tube: a single manifold Σ which reproduces the sphere in the cap region and the tube outside. Let us use the following manifold:

$$\vec{R}(\rho(z)\cos\varphi, \rho(z)\sin\varphi, z),\ \rho(z) = R_t\sqrt{1-\exp(-2\Lambda)}, \tag{11}$$

with

$$\Lambda = \frac{z+R_f}{R_f},\ \alpha = R_t/R_f,\ z \geq -R_f,\ 0 \leq \varphi < 2\pi,$$

where R_f characterizes the capped area and R_t is the tube radius. It is taken into account that R_f can generally be different from R_t. To simplify the problem, one can approximate $S = 2\pi\Lambda$ as if the surface would be the hemisphere with the radius R_f. The metric tensor is written as

$$g_{zz} = \alpha^2\frac{e^{-4\Lambda}}{1-e^{-2\Lambda}} + 1, \quad g_{\varphi\varphi} = \rho^2(z), \quad g_{z\varphi} = 0. \tag{12}$$

The nonzero metric connection coefficients are found to be

$$\begin{aligned}\Gamma^z_{zz} &= \frac{-1}{R_f g_{zz}}(2(g_{zz}-1) + \frac{e^{2\Lambda}}{\alpha^2}(g_{zz}-1)^2),\\ \Gamma^z_{\varphi\varphi} &= -\frac{R_t^2 e^{-2\Lambda}}{R_f g_{zz}}, \quad \Gamma^\varphi_{z\varphi} = \Gamma^\varphi_{\varphi z} = \frac{R_t^2 e^{-2\Lambda}}{R_f g_{\varphi\varphi}}.\end{aligned} \tag{13}$$

The zweibeins are $e^1_z = \sqrt{g_{zz}}$, $e^2_\varphi = \rho(z)$, and the spin connection coefficients are $\omega^{12}_\varphi = -\omega^{21}_\varphi = \alpha R_t e^{-2\Lambda}/(\rho(z)\sqrt{g_{zz}})$, so that (1) include the spin connection term

$$\Omega_\varphi = \frac{i\sigma_3\alpha R_t e^{-2\Lambda}}{2\rho(z)\sqrt{g_{zz}}}. \tag{14}$$

Notice that for $-R_f < z < 0$ the fields are (9), and for $z > 0$ (10). After the substitution $\psi = \begin{pmatrix} u \\ v \end{pmatrix} e^{ij\varphi}$ the Dirac equation (1) takes the form

$$\begin{aligned}-i(\frac{\partial_z}{\sqrt{g_{zz}}} + \frac{1}{\rho(z)}(j - \frac{\alpha R_t e^{-2\Lambda}}{\rho(z)\sqrt{g_{zz}}} - W_\varphi - a_\varphi))v = Eu,\\ -i(\frac{\partial_z}{\sqrt{g_{zz}}} - \frac{1}{\rho(z)}(j + \frac{\alpha R_t e^{-2\Lambda}}{\rho(z)\sqrt{g_{zz}}} - W_\varphi - a_\varphi))u = Ev.\end{aligned} \tag{15}$$

Notice that the momentum j takes half-integer values and enters (15) only by the combination $j - a_\varphi$. We expect that in the tube region our model should be identical to that proposed in [10]. Indeed, adding $\pm 3/2$ to both j and a_φ, one obtains in (10) $\int_0^{2\pi} a_\varphi d\varphi = \pm 2\pi M_2/3$. Exactly such circulation was suggested in [10] for the effective vector potential.

For large z one has $W_\varphi = 0,\ a_\varphi = M_2/3, \sqrt{g_{zz}} \to 1, \rho(z) \to R_t, \Omega_\varphi \to 0$. In this case, (15) takes a similar to [10] form $-i\sigma_1\partial_z\psi + \sigma_2 m\psi = E\psi$, where $E = \pm\sqrt{m^2+k^2}$ and the "mass" term $m = -(j - M_2/3)/R_t$. In this case, the general solution to (15) is written as

$$\psi_k = C\begin{pmatrix} 1 \\ (k-im)/E \end{pmatrix} e^{ikz}, \tag{16}$$

with C being a normalization constant. This plane wave solution has nonzero current $j_z = \bar{\psi}\sigma_1\psi$ which is valid for the infinite tube. In our case, however, the tube is capped and the quasi-particles are not able to leave the tube. For this reason, the current has to be zero everywhere. Taking the condition $j_z = 0$ into account we obtain from (16) the standing wave solution ($\psi_0 = \psi_k + \psi_{-k}$) with zero current

$$\psi_0 = 2C \begin{pmatrix} \cos(kz+\phi) \\ i(k\sin(kz+\phi) - m\cos(kz+\phi))/E \end{pmatrix}. \tag{17}$$

Let us analyze the cap region. For small Λ one has $\rho = R_t\sqrt{2\Lambda}, \sqrt{g_{zz}} = \alpha/\sqrt{2\Lambda}, W_\varphi = -1, a_\varphi = \pm 3/2$ and the equations (15) are written as

$$\begin{aligned} -i(\sqrt{2\Lambda}\partial_\Lambda + \frac{1}{\sqrt{2\Lambda}}(j - B - 1/2))v = \varepsilon u, \\ -i(\sqrt{2\Lambda}\partial_\Lambda - \frac{1}{\sqrt{2\Lambda}}(j - B + 1/2))u = \varepsilon v, \end{aligned} \tag{18}$$

with $B = -1 \pm 3/2$, $\varepsilon = ER_t$. Notice that (18) are similar to the equations for spherical fullerene [5]. At $\Lambda \approx 0$ the general solutions (for both u and v) have a power-like form $C_1\Lambda^\alpha + C_2\Lambda^{-\alpha}$, $\alpha \geq 1/2$. Since the second term cannot be normalized, one has to put $C_2 = 0$.

In the general case, the system (15) can be solved numerically. To this end, the initial conditions are taken to be (17) for $z >> R_f$, and the convergence of the wavefunction at $z = -R_f$ is obtained by a variation of the phase ϕ up to the moment when C_2 turns out to be zero within calculation accuracy. The wavefunction is properly normalized, which means $C = \sqrt{DoS_0(E)}$ where $DoS_0(E) = (\partial E/\partial k)^{-1}$ is the density of states in the infinite tube. The results of numerical calculations are presented in figs.1 and 2.

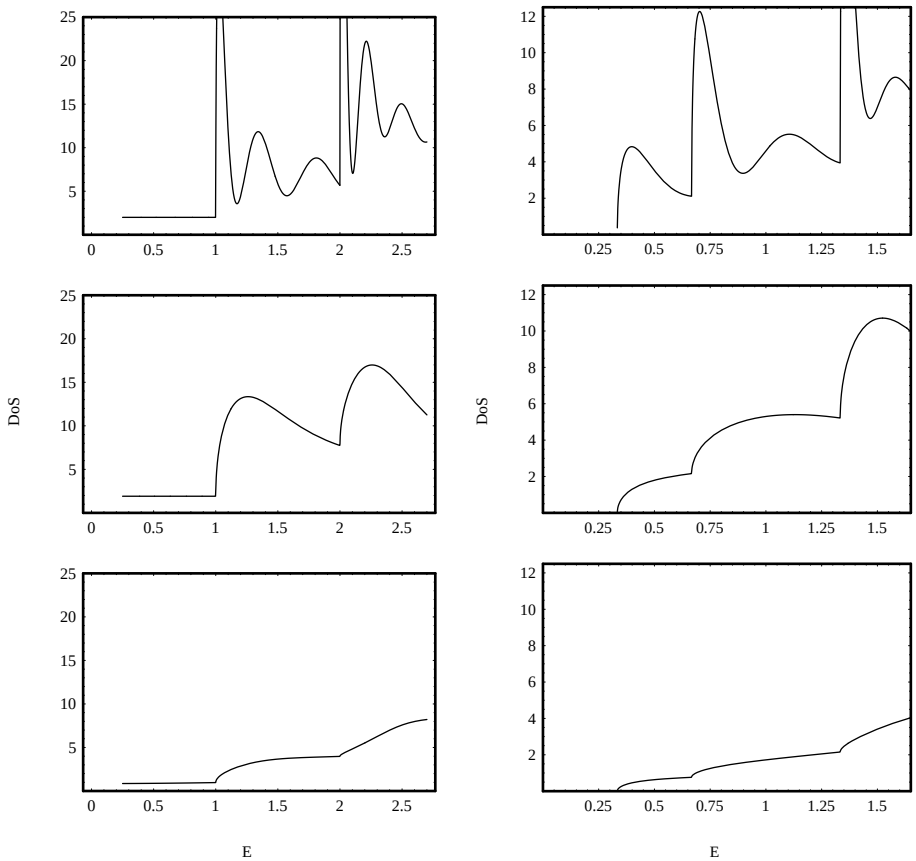

FIG. 2. The density of states (per unit area, in arbitrary units) as a function of the energy in the cap region (bottom), near the cap (middle) and far from the cap (top). The case of metallic (left) and semiconducting (right) tubes is presented. We take $1/\alpha$=0.9, and the energy E is measured in the units of $\hbar V_F/R_t$.

Fig. 2 shows the density of electronic states as a function of the energy in three regions: far from the cap, near the cap and on the cap for both metallic and semiconducting cases. As is seen, the peaks appear at the energies higher than the threshold energy m, where $mR_t = 0, \pm 1, \pm 2, ..$ for metallic and $mR_t = \pm 1/3, \pm 2/3, \pm 4/3, ..$ for semiconducting case. Notice the appearance of secondary (less pronounced) peaks far from the cap. For metallic tube, the constant DoS below the threshold energy is found.

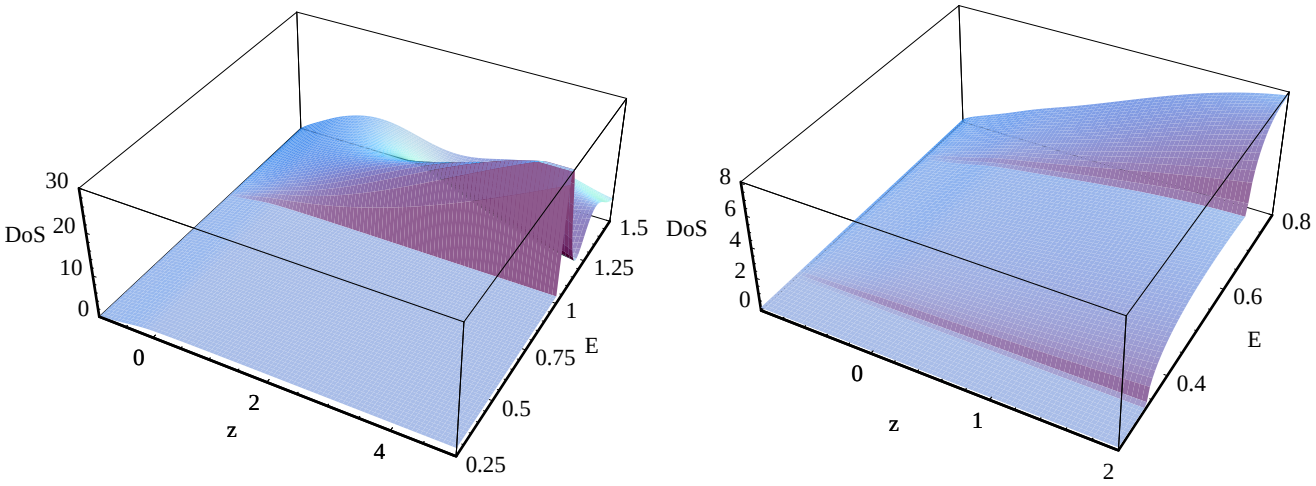

FIG. 3. The density of states (per unit area, in arbitrary units) as a function of the energy (in units of $\hbar V_F/R_t$) and the coordinate (in units of R_t).

Fig. 3 shows the DoS as a function of the energy and the coordinate. In the cap region, both the peak values and the constant DoS (in metallic nanotubes) decrease markedly. At high energies, the harmonic dependence from the coordinate is seen in fig.3 (left), which is in accordance with (17).

The most interesting finding is the finite values of the DoS near points $E = m$ where the DoS behaves linearly in $E - m$. Moreover, as is seen from figs. 2, 3, the smoothed VHS peaks are shifted to higher energies. Within our model the dispersion relation has the form $E = \sqrt{k^2 + m^2}$ and, therefore, $DoS_0(E)$ should diverge like $(E - m)^{-1/2}$ when the energy approaches the threshold m. One could expect a similar behavior in numerical calculations but this was not observed. It should be noted that the only way to avoid the singularity is to put $\phi = \pm\pi/2$ in (17). In this case both spinor components turn out to be finite at $E \approx m$ (both u and v become proportional to k). Thus, the numerical results clearly indicate that the phase is fixed

$$\lim_{E \to m+0} \phi(E) = \pm\pi/2. \tag{19}$$

Let us proof this analytically. Approaching to the cap, the tube tends to decrease its radius which results in a corresponding increase of the effective mass. Using the substitution $\psi = f(\Lambda)\widetilde{\psi}$ where $f(\Lambda) = \exp(-\alpha e^{-2\Lambda}/2)$ and expanding the equations (15) at large Λ up to the order of $e^{-2\Lambda}$ one obtains

$$-i(\partial_\Lambda \mp \mu(1 + e^{-2\Lambda}/2)) \begin{pmatrix} \widetilde{u} \\ \widetilde{v} \end{pmatrix} = \epsilon \begin{pmatrix} \widetilde{u} \\ \widetilde{v} \end{pmatrix}, \tag{20}$$

where $\epsilon = ER_t/\alpha$, $\mu = (M_2/3 - j)/\alpha$. This system is easily reduced to two decoupled equations of the second order

$$\partial_\Lambda^2 \Psi + (Ae^{-2\Lambda} + \kappa^2)\Psi = 0, \tag{21}$$

where $\kappa^2 = \epsilon^2 - \mu^2$, $A = -(\mu^2 \pm \mu)$ where the sign plus (minus) relates to $\Psi = \widetilde{u}$ ($\widetilde{v}$), respectively. In view of $M_2 = 0, \pm 1/3$, $j = \pm 1, \pm 2, ..$ and $\alpha \approx 1$ the constants A for $\widetilde{u}$ and $\widetilde{v}$ always take opposite signs. For positive A (which, for example, relates to $\widetilde{v}$), the substitution $x = \sqrt{A_v}e^{-\Lambda}$ in (21) leads to the Bessel equation of index $i\kappa$

$$x^2\widetilde{v}'' + x\widetilde{v}' + (x^2 + \kappa^2)\widetilde{v} = 0, \tag{22}$$

and for $\widetilde{u}$ there appears the modified Bessel equation (with the argument $x = i\sqrt{|A_u|}e^{-\Lambda}$). The solutions should not diverge at $z \to \infty$ ($x \to 0$), so that they are the Bessel and modified Bessel functions of the first kind, respectively. For small k (but $kz \gg 1$) one has in the leading order

$$\widetilde{v} \approx iC_v\kappa \log x = iC_v kz,$$
$$\widetilde{u} \approx iC_u\kappa \log x = iC_u kz. \tag{23}$$

Substituting this into (20) one obtains the exact relation $iC_v = C_u$ or $iv = u$ in (17), which determines the limit of the phase at $E \to m$ explicitly as $\phi = \pi/2$. Assuming a smooth dependence of the phase ϕ on the energy in (17) we obtain both the high peak at $E > m$ and the linear dependence of the DoS near $E = m$. The amplitude of the peak is found to grow with increasing z (cf. fig. 3).

In conclusion, we have developed a phenomenological model for the description of electronic states in capped nanotubes, both semiconducting and metallic. The influence of pentagons in the cap region was taken into account via the fictitious compensating gauge fields. We have suggested a single manifold for the description of both the nanotube and the cap region. It should be noted that a similar approach was recently used in [12] for the description of both curved and defect-free regions in graphene. The asymptotical solutions in the tube region were used to obtain the initial conditions for the numerical calculations of the density of states. The numerical calculations show that the VHS is smoothed out in DoS. This is explained by the fact that the phase of the wavefunction in the tube region is determined by the asymptotic solution near the cap. As it was analytically shown, in the cap region the mass factor in (20) markedly increases due to geometry. This results in fixation of the wave-function phase which, in turn, provides the smoothing of VHS. Thus, the effect of VHS smoothing is geometrical in its origin within our approach.

The numerical calculations show the finite peaks at energies greater than the threshold energies. The amplitude of the peaks grows with z. At threshold points $E = m$, the DoS is found to be linear in $E - m$ rather than manifests the standard singular behaviour. The obtained results are in qualitative agreement with the experimental measurements and tight-binding calculations for the closed nanotube performed in [3]. At the same time, near the cap an increase of DoS was observed and explained in [3] by the specific distribution of six pentagons on the non-spherical cap. Notice that in our model the defects in the cap region are taken into account by effective continuous fields. For this reason, the localized states are smeared out and there are no pronounced peaks. Between the peak energies the DoS on the cap was found to be reduced in comparison with the tube region [3]. In our model the decrease of the DoS on the cap is found at all energies.

ACKNOWLEDGMENTS

This work has been supported by the Russian Foundation for Basic Research under grant No. 05-02-17721.

---

[1] Tamura R. and Tsukada M. Phys.Rev. B 52 1995 6015
[2] Carroll D.L. et al. Phys. Rev. Lett. 78 1997 2811
[3] Kim P., Odom T. W. et al. Phys. Rev. Lett. 82 1999 1225
[4] Rubio A. Appl. Phys. A 68 1999 275
[5] Kolesnikov D.V. and Osipov V.A. Eur. Phys. J. B 49 2006 465
[6] Osipov V.A. Phys. Lett. A 164 1992 327
[7] Kochetov E.A. and Osipov V.A. J.Phys. A: Math.Gen. 32 1999 1961
[8] González J., Guinea F. and Vozmediano M.A.H. Nucl.Phys. B 406 1993 771
[9] Lammert P.E. and Crespi V.H. Phys. Rev. B 69 2004 035406
[10] Kane C.L. and Mele E.J. Phys. Rev. Lett. 78 1997 1932
[11] González J., Guinea F. and Vozmediano M.A.H. Phys. Rev. Lett. 69 1992 172
[12] Cortijo A., Vozmediano M.A.H. cond-mat/0603717, to be published in Eur.Phys.Lett 2007